

PATENT COOPERATION TREATY

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>P00NM-085W0</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/JP 00/08180</b>	International filing date (day/month/year) <b>21/11/2000</b>	(Earliest) Priority Date (day/month/year) <b>26/11/1999</b>
Applicant  <b>NISSAN MOTOR CO., LTD. et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**.

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.



## INTERNATIONAL SEARCH REPORT

International Application No

T/JP 00/08180

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 B01D53/94 B01J29/04		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 7 B01D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) WPI Data, EPO-Internal, PAJ		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 852 966 A (TOYOTA MOTOR CO LTD) 15 July 1998 (1998-07-15)  page 4, line 29 -page 8, column 29 page 17, line 18 -page 18, line 36; figures 12-16; examples 12-15,22 ---	1,2,5-7, 11,12, 15,16
X	EP 0 782 880 A (NGK INSULATORS LTD) 9 July 1997 (1997-07-09)  page 3, line 32 -page 6, line 43; example 16; tables 1,2,4 page 14, line 17 - line 20; figure 1E --- -/--	1-4, 6-10,12, 13,15,16
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family		
Date of the actual completion of the international search  12 March 2001		Date of mailing of the international search report  16/03/2001
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  Eijkenboom, A



## INTERNATIONAL SEARCH REPORT

International Application No

T/JP 00/08180

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 676 912 A (SHARMA SANJAY B ET AL) 14 October 1997 (1997-10-14) column 2, line 56 - line 60 column 4, line 8 - line 52 column 8, line 52 -column 10, line 42 column 13, line 18 - line 6 -----	1-10,12, 16
X	EP 0 002 791 A (UNION CARBIDE CORP) 11 July 1979 (1979-07-11) page 3, paragraph 1 -page 6, paragraph 1 page 8, paragraph 3 page 11, paragraph 2 -----	1,2,6-8, 10,12



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 00/08180

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0852966	A	15-07-1998	JP 10192707 A	28-07-1998
			JP 10225636 A	25-08-1998
			JP 11076838 A	23-03-1999
			US 6165429 A	26-12-2000
EP 0782880	A	09-07-1997	JP 8010566 A	16-01-1996
US 5676912	A	14-10-1997	NONE	
EP 0002791	A	11-07-1979	AU 4293178 A	05-07-1979
			JP 54096474 A	30-07-1979





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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/37978 A1

(54) Title: EXHAUST GAS PURIFYING CATALYST

(57) Abstract: An exhaust gas purifying catalyst for purifying exhaust gas discharged from an automotive internal combustion engine. The exhaust gas purifying catalyst comprises a monolithic substrate. A HC adsorbing layer for adsorbing hydrocarbons (HC) is formed on the monolithic substrate. The HC adsorbing layer contains zeolite. A catalytic layer for producing hydrogen (H<sub>2</sub>) and reducing NO<sub>x</sub> is formed on the HC adsorbing layer. The catalytic layer functions to produce hydrogen (H<sub>2</sub>) from at least one of hydrocarbons and carbon monoxide (CO) and to reduce nitrogen oxides (NO<sub>x</sub>) with the produced hydrogen and at least one of hydrocarbons and carbon monoxide in exhaust gas.



## DESCRIPTION

### EXHAUST GAS PURIFYING CATALYST

#### 5 FIELD OF THE INVENTION

This invention relates to improvements in an exhaust gas purifying catalyst, and more particularly to improvements in an exhaust gas purifying catalyst for effectively reducing nitrogen oxides in an oxygen-excessive exhaust gas

#### 10 BACKGROUND TECHNIQUE

Hitherto catalysts for simultaneously oxidizing carbon monoxide (CO) and hydrocarbons (HC) and reducing nitrogen oxides (NO<sub>x</sub>) have been extensively used as exhaust gas purifying catalysts installed to internal combustion engines of automotive vehicles and  
15 the like. A typical example of these catalysts is disclosed in Japanese Patent Publication No. 58-20307, in which an alumina coat layer is formed on a refractory substrate and contains noble metals such as Pd, Pt and/or Rh and additionally contains, as assistant catalyst, oxides of rare earth metal such as Ce and/or La and/or of base metal  
20 such as Ni, if necessary.

However, such a catalyst is largely affected by an exhaust gas temperature and a set air-fuel ratio of the engine, and therefore cannot reduce NO<sub>x</sub> particularly when exhaust gas of the engine is oxygen-excessive (i.e., has an air-fuel ratio leaner than  
25 stoichiometric value). In this regard, Japanese Patent No. 2600429 discloses a so-called rich spike process as a method of reducing NO<sub>x</sub> when exhaust gas of the engine is oxygen-excessive, using a NO<sub>x</sub> reducing catalyst for promoting reduction reaction of NO<sub>x</sub>. In this method, NO<sub>x</sub> is trapped when exhaust gas takes an  
30 oxygen-excessive or lean atmosphere (having the air-fuel ration leaner than the stoichiometric value), and then the trapped NO<sub>x</sub> is released and reduced by temporarily lowering an oxygen concentration of exhaust gas so that exhaust gas takes exhaust gas



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takes a rich atmosphere (having the air-fuel ratio richer than the stoichiometric value).

#### DISCLOSURE OF THE INVENTION

5 Drawbacks have been encountered in the above NOx reducing method using the rich spike process, as set forth below. That is, the NOx reducing method requires to periodically lowering the oxygen concentration in exhaust gas in an engine operating region in which exhaust gas takes the oxygen-excessive atmosphere. Additionally, in order to make reduction reaction of NOx under a  
10 condition where the oxygen concentration has been lowered, it is required to supply a large amount of HC and CO as reducing agents. This makes it impossible to obtain fuel economy improvement effect due to vehicle running on oxygen-excessive air-fuel mixture having an air-fuel ratio leaner than the stoichiometric value.

15 Additionally, in the above NOx reducing method, the catalyst contains a large amount of alkali metal and alkaline earth metal for the purpose of trapping NOx in the oxygen-excessive atmosphere of exhaust gas, and therefore a catalytic activity (for oxidation) of platinum and rhodium cannot be sufficiently exhibited when  
20 exhaust gas is low in temperature. Furthermore, in order to sufficiently oxidize or remove HC and CO components which have not been consumed under NOx reduction reaction, it is required to oxidize or remove the components by making oxidation reaction on the NOx reducing catalyst, or otherwise by a three-way catalyst  
25 disposed downstream of the NOx reducing catalyst for reducing NOx.

However, such the NOx reducing catalyst or the three-way catalyst disposed downstream of the NOx reducing catalyst are located considerably far from the engine, and therefore the temperature of exhaust gas flown to the catalysts are unavoidably  
30 lowered, thereby making it impossible to exhibit a sufficient oxidizing performance for HC and CO. Particularly immediately after engine starting, sufficient oxidation of HC and CO is difficult to be made. Additionally, when HC and CO components in exhaust gas



are increased to lower an oxygen concentration in exhaust gas and to reduce NOx as discussed above, it is impossible to make vehicle running under lean-burn operation, thereby exhibiting an insufficient fuel economy improvement effect.

5           It is, therefore, an object of the present invention is to provide an improved exhaust gas purifying catalyst which can effectively overcome drawbacks encountered in conventional techniques for reducing NOx in exhaust gas.

10           Another object of the present invention is to provide an improved exhaust gas purifying catalyst which can effectively remove NOx, HC and CO from exhaust gas while obtaining a high fuel economy improvement effect.

15           A further object of the present invention is to provide an improved exhaust gas purifying catalyst for an internal combustion engine, which can remove NOx in exhaust gas at a high efficiency by using hydrogen (H<sub>2</sub>) as reducing agent and effectively remove HC and CO particularly during a low temperature engine operation immediately after engine starting, while obtaining a high fuel economy improvement effect upon making lean-burn operation of  
20           the engine.

25           An aspect of the present invention resides in an exhaust gas purifying catalyst comprising a monolithic substrate. A HC adsorbing layer for adsorbing hydrocarbons (HC) is formed on the monolithic substrate. A catalytic layer for producing hydrogen (H<sub>2</sub>) and reducing NOx is formed on the HC adsorbing layer. The catalytic layer functions to produce hydrogen (H<sub>2</sub>) from at least one of hydrocarbons and carbon monoxide (CO) and to reduce nitrogen oxides (NOx) with the produced hydrogen and at least one of hydrocarbons and carbon monoxide in exhaust gas.

30           Another aspect of the present invention resides in an exhaust gas purifying system for an internal combustion engine. The exhaust gas purifying system comprises an exhaust gas purifying catalyst including a monolithic substrate. A HC adsorbing layer for





adsorbing hydrocarbons (HC) is formed on the monolithic substrate.  
A catalytic layer for producing hydrogen ( $H_2$ ) and reducing  $NO_x$  is  
formed on the HC adsorbing layer. The catalytic layer functions to  
produce hydrogen ( $H_2$ ) from at least one of hydrocarbons and carbon  
monoxide (CO) and to reduce nitrogen oxides ( $NO_x$ ) with the  
5 produced hydrogen and at least one of hydrocarbons and carbon  
monoxide in exhaust gas. A device is provided to control combustion  
in the engine to produce exhaust gas, to be brought into contact with  
the catalytic layer, having a composition meeting a relation [(a  
10 concentration of hydrogen / a concentration of total reducing  
components)  $\geq 0.3$ ].

A further aspect of the present invention resides in a  
method of producing an exhaust gas purifying catalyst. The method  
comprises (a) preparing a monolithic substrate; (b) forming a HC  
15 adsorbing layer on the monolithic substrate; (c) forming a catalytic layer  
on the HC adsorbing layer, to adsorb hydrocarbons  
to produce hydrogen ( $H_2$ ) and reduce  $NO_x$ , the catalytic layer  
functioning to produce hydrogen ( $H_2$ ) from at least one of  
hydrocarbons and carbon monoxide (CO) and to reduce nitrogen  
20 oxides ( $NO_x$ ) with the produced hydrogen and at least one of  
hydrocarbons and carbon monoxide in exhaust gas.

#### BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a fragmentary transverse sectional view of an  
example of an exhaust gas purifying catalyst according to the  
25 present invention, showing a coat layer structure defining a cell  
through which exhaust gas flows, and functions of respective layers  
in the structure;

Fig. 2 is a fragmentary longitudinal sectional view of  
another example of an exhaust gas purifying catalyst according to  
30 the present invention, showing a coat layer structure defining a cell  
through which exhaust gas flows, and functions of respective layers  
in the structure;



Fig. 3 is a fragmentary longitudinal sectional view of a further example of an exhaust gas purifying catalyst according to the present invention, showing a coat layer structure defining a cell through which exhaust gas flows, in connection of Examples;

5 Fig. 4 is a fragmentary longitudinal sectional view of a still further example of an exhaust gas purifying catalyst according to the present invention, showing a coat layer structure defining a cell through which exhaust gas flows, in connection of Examples;

10 Fig. 5 is a fragmentary longitudinal sectional view of a still further example of an exhaust gas purifying catalyst according to the present invention, showing a coat layer structure defining a cell through which exhaust gas flows, in connection of Examples; and

Fig. 6 is a schematic illustration of an exhaust gas purifying system (including the exhaust gas purifying catalyst according to the present invention) incorporated with an automotive internal combustion engine, the engine being used as an evaluation engine system for evaluating emission performance of the exhaust gas purifying catalysts according to the present invention.

#### THE BEST MODE FOR CARRYING OUT THE INVENTION

20 According to the present invention, an exhaust gas purifying catalyst comprises a monolithic substrate. A HC adsorbing layer for adsorbing hydrocarbons (HC) is formed on the monolithic substrate. A catalytic layer for producing hydrogen ( $H_2$ ) and reducing  $NO_x$  is formed on the HC adsorbing layer. The catalytic  
25 layer functions to produce hydrogen ( $H_2$ ) from at least one of hydrocarbons and carbon monoxide (CO) and to reduce nitrogen oxides ( $NO_x$ ) with the produced hydrogen and at least one of hydrocarbons and carbon monoxide in exhaust gas.

The HC adsorbing layer preferably contains zeolite (HC  
30 adsorbing material) capable of adsorbing hydrocarbons, as a main component. In case that the exhaust gas purifying catalyst is for an internal combustion engine, for example, of an automotive vehicle, the HC adsorbing layer can adsorb HC during a cold operation of the

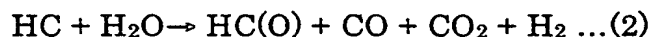
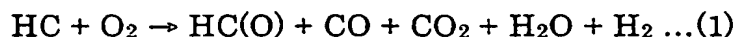


engine, i.e., when the catalyst has been still at a low temperature immediately after engine starting, and release HC during a warm-up operation of the engine, i.e., when the catalyst is at a temperature within a range of from 100 to 300 °C. It will be understood that cold stage and warm-up stages of the catalyst are respectively during the cold operation and the warm-up operation of the engine.

The catalytic layer for producing H<sub>2</sub> and reducing NO<sub>x</sub> functions to produce hydrogen (H<sub>2</sub>) from hydrocarbons released from the HC adsorbing layer under reforming reactions of HC and CO as discussed below. Additionally, the catalytic layer functions also to produce hydrogen (H<sub>2</sub>) from hydrocarbons and/or carbon monoxide in exhaust gas discharged from the engine during a steady state engine operation. Hydrogen (H<sub>2</sub>) thus produced can effectively react with NO<sub>x</sub>, serving as reducing agent.

It is to noted that reactivity of hydrogen with NO<sub>x</sub> is high, and therefore it is assumed that NO<sub>x</sub> emitted from the engine can be effectively reduced even during the warm-up stage of from a time immediately after the engine starting to a time making lean-burn operation of the engine although the NO<sub>x</sub> reducing catalyst component contained in the catalytic layer has not been sufficiently raised in temperature and sufficiently activated. In the lean-burn operation, the engine is supplied mainly with air-fuel mixture having an air-fuel ratio leaner than a stoichiometric value, thereby discharging exhaust gas (or oxygen-excessive atmosphere) having an air-fuel ratio leaner than a stoichiometric value.

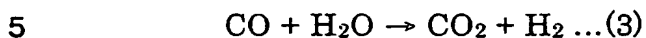
The above HC and CO reforming reactions carried out in the catalytic layer is divided in general into reforming reaction of HC and steam reforming reaction of CO. The HC reforming reaction is assumed to be represented by the following reaction formulae (1) and (2):





where HC(O) indicates HC produced under the reforming reaction of HC.

The CO steam reforming reaction is assumed to be represented by the following reaction formula (3):



The catalytic layer contains a H<sub>2</sub> producing catalyst component for functioning to produce hydrocarbons, and a NO<sub>x</sub> reducing catalyst component for functioning to reduce nitrogen oxides. The H<sub>2</sub> producing catalyst component is disposed on the HC adsorbing layer and including a HC reforming catalyst component functioning to reform hydrocarbons so as to produce hydrogen, and a CO reforming catalyst component functioning to make steam reforming of carbon monoxide. The HC reforming catalyst component preferably contains cerium oxide carrying palladium.

10                    The CO reforming catalyst component preferably contains zirconium oxide carrying rhodium.

15                   

Preferably, the HC reforming catalyst component forms a first layer disposed on the monolithic substrate, and the CO reforming catalyst forms a second layer, in which the second layer is formed on the first layer, so that the catalytic layer takes a multiple layer structure. Otherwise, the HC reforming catalyst component and the CO reforming catalyst are mixed to form a single layer disposed on the monolithic substrate on the HC adsorbing layer, so that the catalytic layer takes a single layer structure. Otherwise, the HC reforming catalyst component forms a first layer disposed on the monolithic substrate, and the CO reforming catalyst component forms a second layer, in which the second layer is formed downstream of the first layer relative to flow direction of exhaust gas.

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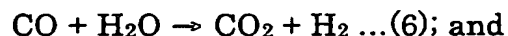
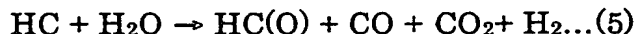
30                    As shown in Fig. 1, HC adsorbed in the HC adsorbing layer immediately after engine starting and released from the HC adsorbing layer at the warm-up stage of the catalyst is first subjected to partial oxidation in the HC reforming layer so that HC



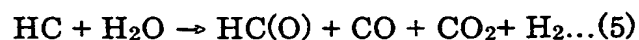


is converted into partial oxide (HC(O) corresponding to partially oxidized HC), CO and H<sub>2</sub>. Then, the partial oxide, CO and H<sub>2</sub> are converted into H<sub>2</sub> in the CO reforming layer. As a result, even at the catalyst warm-up stage, H<sub>2</sub> is produced under reforming of HC and CO, and therefore NO<sub>x</sub> can be reduced. Additionally, during an engine operating range accomplishing the lean-burn operation, H<sub>2</sub> is supplied in the catalytic layer, thereby reducing NO<sub>x</sub> after completion of the catalyst warm-up. It will be understood that the HC reforming layer and the CO reforming layer may be arranged side by side (or located respectively on the upstream and downstream sides) in a direction of flow of exhaust gas since it is sufficient that HC released from the HC adsorbing layer undergoes first the HC reforming reactions, and subsequently the CO steam reforming reaction.

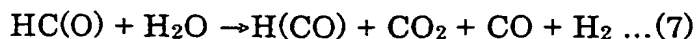
Additionally, in order to produce H<sub>2</sub> under reforming of HC, it is preferable that the above-discussed HC reforming layer contains cerium oxide carrying Pd. In order to produce H<sub>2</sub> under steam reforming of CO, it is preferable that the above-discussed CO reforming layer contains zirconium oxide carrying Rd. By virtue of these noble metals and oxides contained, reactions represented by the following formulae (4), (5) and (6) are assumed to be mainly carried out in the HC reforming layer when exhaust gas is introduced or passed into the exhaust gas purifying catalyst of the present invention:



Additionally, reactions represented by the following formulae (5), (6) and (7) are assumed to be mainly carried out in the CO reforming layer when exhaust gas is introduced or passed into the exhaust gas purifying catalyst of the present invention:







As a result of the above reactions,  $\text{H}_2$  is produced while exhaust gas components, particularly HC and CO are oxidized to be removed.

5 Further, the catalytic layer for producing  $\text{H}_2$  and reducing NOx contains not only the catalyst components for producing  $\text{H}_2$  but also the catalyst components for reducing NOx. Thus, even with such a single catalyst,  $\text{H}_2$  serving as the reducing agent for NOx can be produced while effectively reducing NOx.

10 Furthermore, in order to further promote production of  $\text{H}_2$  from HC and CO in exhaust gas even after the engine warm-up stage, it is preferable that an upstream section of the catalytic layer for producing  $\text{H}_2$  and reducing NOx is replaced with a catalytic (upstream) layer containing alumina carrying Pd. The upstream  
15 section is located at an upstream side with respect to flow of exhaust gas discharged from the engine. More specifically, such a preferable mode is as follows: A HC partial oxidation or reforming layer containing alumina carrying Pd is formed on the upstream side or section of the HC adsorbing layer while the HC reforming layer  
20 containing cerium oxide carrying Pd and the CO reforming layer containing zirconium oxide carrying Pd are formed on a downstream side or section of the HC adsorbing layer.

An example of this preferable mode is shown in Fig. 2; however, the exhaust gas purifying catalyst of the present invention  
25 is not limited to this example. In the example of Fig. 2, the CO reforming layer is formed on the HC reforming layer on the downstream side or section of the HC adsorbing layer. Additionally, the HC partial oxidation layer on the upstream side or section of the HC adsorbing layer is in contact with the HC reforming layer and  
30 the CO reforming layer on the downstream side or section of the HC adsorbing layer. In the exhaust gas purifying catalyst as shown in Fig. 2, after the warm-up stage of the catalyst, it is assumed that the HC partial oxidation layer (containing alumina carrying Pd) on the



upstream side or section converts HC contained in exhaust gas into HC(O) and CO under partial oxidation; then the HC reforming layer promotes production of H<sub>2</sub> under the reforming reaction of H(CO); and subsequently the CO reforming layer produces H<sub>2</sub> under steam  
5 reforming reaction of CO. Accordingly, according to this example, H<sub>2</sub> can be supplied even after completion of warm-up of the catalyst, subsequent to the warm-up stage of the catalyst. This makes it possible to reduce and remove NO<sub>x</sub> in exhaust gas having the lean air-fuel ratio or in the oxygen-excess atmosphere.

10 As discussed above, in operation of the exhaust gas purifying catalyst of the present invention, H<sub>2</sub> is used as the reducing agent, in place of HC and CO which have been conventionally used as reducing agent. In this connection, it is preferable that composition of exhaust gas to be brought into contact  
15 with the NO<sub>x</sub> reducing catalyst component meets a relation [(a concentration of hydrogen / a concentration of total reducing components)  $\geq$  0.3]. Such exhaust gas composition meeting the above relation can be realized, for example, by controlling combustion to be made in combustion chambers of an internal combustion engine, i.e.,  
20 by controlling fuel injection amount (amount of fuel injected from a fuel injector), fuel injection timing (timing at which fuel is injected from the fuel injector), spark timing (timing at which a spark plug generates spark), opening and/or closing timings of intake and/or exhaust valves.

25 For example, as shown in Fig. 6, the above relation in exhaust gas was accomplished by controlling the fuel injection amount and fuel injection timing of fuel to be injected from a fuel injection system 11 by control signals fed from an electronic control unit (ECU) 13. The electronic control unit 13 is arranged to be  
30 supplied with signals representative of intake air amount (amount of air to be sucked into the engine), combustion pressure (pressure within combustion chamber under combustion) and exhaust gas temperature (temperature of exhaust gas discharged from the



engine), and signals of a temperature sensor for detecting, for example, temperature of engine coolant, an engine speed sensor for detecting engine speed of the engine, and an air flow sensor for detecting amount of air flowing into the engine, and an oxygen  
5 sensor 12 for detecting an oxygen concentration in an exhaust gas passageway 10a through which exhaust gas from the engine flows to be emitted to the atmosphere. In Fig. 6, a upstream-side catalyst 1 and a downstream-side catalyst 2 are disposed in the exhaust gas passageway 10a. The oxygen sensor 12 is located in the exhaust gas  
10 passageway 10a between the upstream-side and downstream-side catalysts 1, 2.

When the exhaust gas composition can meet the relation resented by the above relation, the concentration of  $H_2$  in exhaust gas rises thereby obtaining a further high  $NO_x$  reducing  
15 performance. In this connection, in conventional techniques, exhaust gas from automotive engines or from exhaust systems including exhaust gas purifying catalysts has a relation [(a concentration of hydrogen / a concentration of total reducing components)  $< 0.3$ ]. Consequently, the rate or concentration of  $H_2$  in  
20 exhaust gas is considerably small so that it is impossible to effectively use  $H_2$  as reducing component or agent.

Additionally, it is more preferable that the composition of exhaust gas to be brought into contact with the  $NO_x$  reducing catalyst component meets the relation [(a concentration of hydrogen  
25 / a concentration of total reducing components)  $\geq 0.5$ ].

In the above CO reforming layer, in order to maintain oxidizing condition of Rh suitable for CO steam reforming reaction, it is preferable that the above-mentioned zirconium oxide carrying Rd contains alkaline earth and has a composition represented by the  
30 following formula (A):



where X is an alkaline earth metal selected from the group consisting of magnesium, calcium, strontium and barium; a and b





are ratios of atoms of elements; and  $c$  is a number of oxygen atoms required for satisfying valences of  $X$  and  $Zr$ , in which  $a$  is within a range of from 0.01 to 0.5,  $b$  is within a range of from 0.5 to 0.99, and  $a+b = 1.0$ .

5           It is to be noted that the alkaline earth metal contained in the zirconium oxide makes it possible to obtain a high catalytic activity throughout a long time use (including the initial time in use).

10           Additionally, it is preferable that the  $NO_x$  reducing catalyst component for reducing  $NO_x$  is contained in at least one of the HC adsorbing layer, the catalytic layer for producing  $H_2$  and reducing  $NO_x$  and the upstream side catalytic layer containing alumina carrying Pd. Accordingly, Pt and/or Rh serving as the  $NO_x$  reducing catalyst components may be contained in all of the HC  
15 adsorbing layer, the HC reforming layer, the CO reforming layer of the catalytic layer for producing  $H_2$  and reducing  $NO_x$ , and the upstream-side catalytic layer containing alumina carrying Pd. By virtue of the  $NO_x$  reducing catalyst component,  $H_2$  can be produced in the warm-up stage of the catalyst while  $NO_x$  emitted in the  
20 catalyst warm-up stage can be effectively reduced and removed. Additionally,  $NO_x$  emitted can be also effectively reduced and removed during engine operational control under supply of air-fuel mixture having lean air-fuel ratio to the engine (i.e., the oxygen-excess atmosphere).

25           In addition to the fact that the  $NO_x$  reducing catalyst component is contained in at least one of the respective catalytic layers, it is also preferable that a further catalytic layer for reducing  $NO_x$  may be formed on the catalytic layer for producing  $H_2$  and reducing  $NO_x$ . Otherwise, the further catalytic layer may be formed  
30 on the catalytic layer for producing  $H_2$  and reducing  $NO_x$  without the  $NO_x$  reducing catalyst component being contained in at least one of the respective catalytic layers. Otherwise, the exhaust gas purifying catalyst of the present invention may be disposed



upstream of a NOx reducing catalyst in the exhaust gas passageway through which exhaust gas discharged from the engine flows.

Furthermore, the NOx reducing catalyst component including Pd, alumina, alkali metal(s) and/or alkaline earth metal(s) may be contained in at least one of the HC adsorption layer, the HC partial oxidation layer, the CO reforming layer and/or the upstream section of the catalytic layer. By virtue of the above NOx reducing catalyst component contained in the exhaust purifying catalyst, NOx emitted from the engine can be effectively reduced and removed throughout whole engine operating regions from a time immediately after engine starting to a time accomplishing a steady state engine operation providing the oxygen-excess atmosphere.

It is preferable that the content of the above alkali metal(s) and/or alkaline earth metal(s) in the whole catalytic layer (formed on the HC adsorbing layer) is not less than 80 % by weight of a total content of alkali metal(s) and alkaline earth metal(s) contained in the exhaust gas purifying catalyst. With such a content, NOx emitted from the engine can be effectively trapped by the alkali metal(s) and/or alkaline earth metal(s) in a lean region (in which exhaust gas has air-fuel ratio leaner than stoichiometric level). If the content is less than 80 % by weight, a sufficient NOx trapping performance cannot be obtained.

In order to realize the above content (of 80 % by weight) of alkali metal(s) and/or alkaline earth metal(s), it is preferable that the alkali metal(s) and/or alkaline earth metal(s) are used as water-insoluble compound(s) and/or slightly water-soluble compound(s).

Zeolite used in the above HC adsorbing layer is selected from known zeolites; however, it is preferable to select zeolite(s) which can exhibit a sufficient HC adsorbing performance particularly in a temperature region of from ordinary temperature to a relatively high temperature and even in an atmosphere in presence of water, and a high durability. A preferable example of



such zeolites is H-type  $\beta$ -zeolite having a Si/2Al ratio ranging from 10 to 500; however, zeolite to be used in the HC adsorbing layer is not limited to this. If zeolite has a Si/2Al ratio smaller than 10, it cannot effectively adsorb HC because impeding HC adsorption by  
5 water coexisting in exhaust gas is considerable. If zeolite has a Si/2Al ratio larger than 500, HC adsorbing performance of zeolite may be lowered.

Furthermore, it is also preferable to select at least one of MFI, Y-type zeolite, USY-type zeolite and/or mordenite which are  
10 different from each other in diameter and structure of fine pores formed in the zeolite, and to mix the selected one(s) with the above-mentioned H-type  $\beta$ -zeolite so as to prepare the zeolite to be contained in the HC adsorbing layer. Such selection is made taking account of the components of exhaust gas discharged from the engine,  
15 resulting in effective adsorption of HC in the HC adsorbing layer.

It will be understood that the above H-type  $\beta$ -zeolite has a sufficient HC adsorption performance; however, the H-type  $\beta$ -zeolite may carry Pd, Mg, Ca, Sr, Ba, Ag, Y, La, Ce, Nd, P, B and/or Zr by using conventional methods such as an ion exchange method, an  
20 impregnation method or a dipping method, thereby further improving HC adsorption performance and HC release-suppression performance of the zeolite.

An example of the monolithic substrate used in the exhaust gas purifying catalyst is a honeycomb-type monolithic  
25 substrate. The honeycomb-type monolithic substrate is formed of ceramic materials such as cordierite ceramic, or may be formed of metal such as ferrite stainless steel. Otherwise, powder serving as the catalyst components may be formed into a honeycomb shape. The honeycomb-type monolithic substrate is formed with a plurality of  
30 cells which axially extend. Each cell is defined by walls which axially extend and have a thickness

#### EXAMPLES



The present invention will be more readily understood with reference to the following Examples in comparison with Comparative Example; however, these Examples are intended to illustrate the invention and are not to be construed to limit the scope of the invention.

[Preparation of Catalytic Powder of HC Reforming Layer]

Cerium oxide ( $\text{CeO}_2$ ) powder was impregnated with an aqueous solution of palladium (Pd) nitrate, followed by drying and firing, thereby preparing Pd-carried cerium oxide powder A whose concentration of Pd was 10 % by weight.

Subsequently, powder B was prepared by repeating the same operation as that for Powder A with the exception that  $\text{Zr}_{0.1}\text{Ce}_{0.9}\text{O}_2$  was used in place of  $\text{CeO}_2$ .

Powder C was prepared by repeating the same operation as that for Powder A with the exception that  $\text{Zr}_{0.2}\text{Ce}_{0.8}\text{O}_2$  was used in place of  $\text{CeO}_2$ .

Powder D was prepared by repeating the same operation as that for Powder A with the exception that  $\text{Zr}_{0.5}\text{Ce}_{0.5}\text{O}_2$  was used in place of  $\text{CeO}_2$ .

Powder E was prepared by repeating the same operation as that for Powder A with the exception that  $\text{Zr}_{0.9}\text{Ce}_{0.1}\text{O}_2$  was used in place of  $\text{CeO}_2$ .

Powder F was prepared by repeating the same operation as that for Powder A with the exception that Powder F had a Pd concentration of 5 % by weight.

[Preparation of Catalytic Powder for CO Reforming Layer]

Powder of  $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$  was impregnated with an aqueous solution of rhodium (Rh) nitrate, followed by drying and firing, thereby preparing Rh-carried zirconium oxide powder G whose Rh concentration was 6 % by weight.

Subsequently, Powder H was prepared by repeating the same operation as that for Powder G with the exception that powder of  $\text{Mg}_{0.1}\text{Zr}_{0.9}\text{O}_2$  was used in place of the powder of  $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$ .





Powder I was prepared by repeating the same operation as that for Powder G with the exception that powder of  $\text{Ba}_{0.1}\text{Zr}_{0.9}\text{O}_2$  was used in place of the powder of  $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$ .

5 Powder J was prepared by repeating the same operation as that for Powder G with the exception that powder of  $\text{Sr}_{0.2}\text{Zr}_{0.8}\text{O}_2$  was used in place of the powder of  $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$ .

Powder K was prepared by repeating the same operation as that for Powder G with the exception that powder  $\text{Ca}_{0.1}\text{Mg}_{0.1}\text{Zr}_{0.8}\text{O}_2$  was used in place of the powder of  $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$ .

10 Powder L was prepared by repeating the same operation as that for Powder G with the exception that powder  $\text{Ca}_{0.1}\text{Ba}_{0.05}\text{Mg}_{0.05}\text{Zr}_{0.8}\text{O}_2$  was used in place of the powder of  $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$ .

Powder M was prepared by repeating the same operation as that for Powder G with the exception that powder  $\text{Ca}_{0.01}\text{Zr}_{0.99}\text{O}_2$  was used in place of the powder of  $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$ .

Powder N was prepared by repeating the same operation as that for Powder G with the exception that powder  $\text{Ca}_{0.55}\text{Zr}_{0.45}\text{O}_2$  was used in place of the powder of  $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$ .

[Preparation of Catalytic Powder of HC oxidizing layer]

20 Powder of activated alumina ( $\text{Al}_2\text{O}_3$ ) was impregnated with an aqueous solution of palladium (Pd) nitrate, followed by drying and firing, thereby preparing Pd-carried alumina powder O whose Pd concentration was 15 % by weight.

25 Subsequently, powder P was prepared by repeating the same operation as that for powder O with the exception that powder of powder of activated alumina ( $\text{Al}_2\text{O}_3$ ) containing 3 % by weight of Ce was used in place of the powder of  $\text{Al}_2\text{O}_3$ .

Powder Q was prepared by repeating the same operation as that for powder O with the exception that powder of activated alumina ( $\text{Al}_2\text{O}_3$ ) containing 3 % by weight of Zr was used in place of the powder of  $\text{Al}_2\text{O}_3$ .

Powder R was prepared by repeating the same operation as that for powder O with the exception that powder of alumina



(Al<sub>2</sub>O<sub>3</sub>) containing 3 % by weight of La was used in place of the powder of Al<sub>2</sub>O<sub>3</sub>.

Powder S was prepared by repeating the same operation as that for powder O with the exception that powder of alumina (Al<sub>2</sub>O<sub>3</sub>) containing 10 % by weight of Zr was used in place of the powder of Al<sub>2</sub>O<sub>3</sub>.

[Preparation of Catalytic Powder of NO<sub>x</sub> reducing layer]

Powder of activated alumina (Al<sub>2</sub>O<sub>3</sub>) was impregnated with an aqueous solution of palladium (Pd) nitrate, followed by drying and firing, thereby preparing Pd-carried alumina powder T whose Pd concentration was 8 % by weight.

Powder of activated alumina (Al<sub>2</sub>O<sub>3</sub>) was impregnated with an aqueous solution of dinitrodiammine platinum, followed by drying and firing, thereby preparing Pt-carried alumina powder U whose Pt concentration was 6 % by weight.

Powder of activated alumina (Al<sub>2</sub>O<sub>3</sub>) was impregnated with an aqueous solution of rhodium (Rh) nitrate, followed by drying and firing, thereby preparing Rh-carried alumina powder V whose Rh concentration was 4 % by weight.

## EXAMPLE 1

[Preparation of Catalyst]

β-Zeolite (Si/2Al = 25) in an amount of 900 g was mixed with 100 g of silica sol and 1000 g of pure water, followed by pulverizing, thereby forming a slurry. The slurry was coated on a cordierite ceramic honeycomb-type monolithic substrate having a volume of 1.3 liters and 900 cells per square inch and having a thickness of walls (defining each cell) of 4 mil, so that the walls of the cells were coated with the slurry. The thus coated substrate was dried and then fired thereby to obtain a catalyst Z1 having 100 g of a zeolite coat per one liter of the monolithic substrate.

Subsequently, 706 g of the powder A, 14g of nitric acid-acidic alumina binder and 800 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on the



catalyst Z1, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby to obtain a catalyst A provided with a coat formed on the catalyst Z1 and having a weight of 72 g per one liter of the monolithic substrate. The catalyst A carried 7.06 g of Pd per one liter of the monolithic substrate.

Additionally, 588 g of the powder G, 12g of nitric acid-acidic alumina binder and 600 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on the catalyst A, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby to obtain a catalyst AG1 (shown in Table 2) provided with a coat in an amount of 60 g per one liter of the monolithic substrate. The catalyst AG1 carried 3.53 g per one liter of the monolithic substrate. The catalyst AG1 took a three-layer structure as shown in Fig. 3.

In the column of "HC adsorbing layer" in Table 2, " $\beta$  (Si/2Al=25)" indicates the fact that the HC adsorbing layer contained  $\beta$ -zeolite (having a Si/2Al ratio of 25). In the column of "First layer" in Table 2, "A" indicates the fact that the First layer contained the powder A. In the column of "Second layer" in Table 2, "G" indicates the fact that the Second layer contained the powder G.

The HC adsorbing layer, the First layer, the Second layer and the Third layer shown in Table 2 are correspondingly illustrated in Fig. 3.

#### [Preparation of NO<sub>x</sub> reducing Catalyst]

The powder T in an amount of 618 g, 530 g of the powder U, 88 g of the powder V, 20 g of sodium hydroxide (calculated as Na<sub>2</sub>O), 20 g of barium acetate (calculated as BaO), 14 g of nitric acid-acidic alumina binder and 1500 g of pure water were mixed, followed by pulverizing, thereby forming a slurry. This slurry was coated on a cordierite ceramic honeycomb-type monolithic substrate having a volume of 1.3 liters and 400 cells per square inch and having a thickness of walls (defining each cell) of 6 mil, so that the walls of the



cells were coated with the slurry. The thus coated monolithic substrate was dried and fired thereby to obtain a catalyst N1 provided with a coat formed on the monolithic substrate and having a weight of 147 g per one liter of the monolithic substrate. The catalyst N1 carried 4.94 g of Pd, 3.18 g of Pt and 0.35 g of Rh per one liter of the monolithic substrate. The catalyst N1 took such a structure that a single layer of coat was formed on the monolithic substrate.

[Construction of Exhaust Gas Purifying System]

An exhaust gas purifying system of Example 1 was constructed by disposing the catalyst AG1 in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the (NO<sub>x</sub> reducing) catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst AG1 and located at the position of the catalyst 2.

EXAMPLES 2 to 7

[Preparation of Catalyst]

Catalysts AG2, AG4, AG5, AG6 and AG7 (shown in Table 2) corresponding respectively to Examples 2, 3, 4, 5, 6 and 7 were obtained repeating the above preparation operation for the catalyst AG1 with the exception that  $\beta$ -zeolite ( $\text{Si}/2\text{Al} = 25$ ) was replaced with other HC adsorbing materials shown in Table 2, respectively.

In the column of "HC adsorbing layer" in Table 2, " $\beta(\text{Si}/2\text{Al} = 15)$ " indicates the fact that the HC adsorbing layer contained  $\beta$ -zeolite (having a  $\text{Si}/2\text{Al}$  ratio of 15); " $\beta(\text{Si}/2\text{Al} = 300)$ " indicates the fact that the HC adsorbing layer contained  $\beta$ -zeolite (having a  $\text{Si}/2\text{Al}$  ratio of 300); " $\beta(\text{Si}/2\text{Al} = 25) + \text{MFI} (= 30)$ " indicates the fact that the HC adsorbing layer contained a mixture of  $\beta$ -zeolite (having a  $\text{Si}/2\text{Al}$  ratio of 25) and MFI (having a  $\text{Si}/2\text{Al}$  ratio of 30); " $\beta(=25)+\text{USY}(=15)$ " indicates the fact that the HC adsorbing layer contained a mixture of  $\beta$ -zeolite (having a  $\text{Si}/2\text{Al}$  ratio of 25) and USY-type zeolite having a  $\text{Si}/2\text{Al}$  ratio of 15); " $\text{Ag,P-}\beta(=25)$ " indicates the fact that the HC





adsorbing layer contained  $\beta$ -zeolite (having a Si/2Al ratio of 25) containing and P; and "Pd- $\beta$ (=25)" indicates the fact that the HC adsorbing layer contained  $\beta$ -zeolite (having a Si/2Al ratio of 25) containing.

5 [Construction of Exhaust Gas Purifying System]

Each of exhaust gas purifying systems of Examples 2, 3, 4, 5, 6 and 7 was constructed by disposing the catalyst AG2, AG3, AG4, AG5, AG6 or AG7 in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the (NO<sub>x</sub> reducing catalyst) N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst AG2, AG3, AG4, AG5, AG6 or AG7 and located at the position of the catalyst 2.

EXAMPLE 8

15 [[Preparation of Catalyst]

$\beta$ -Zeolite (Si/2Al = 25) in an amount of 900 g was mixed with 100 g of silica sol and 1000 g of pure water, followed by pulverizing, thereby forming a slurry. The slurry was coated on a cordierite ceramic honeycomb-type monolithic substrate having a volume of 1.3 liters and 900 cells per square inch and having a thickness of walls (defining each cell) of 4 mil, so that the walls of the cells were coated with the slurry. The thus coated substrate was dried and then fired thereby to obtain a catalyst Z1 having 100 g of a zeolite coat per one liter of the monolithic substrate.

Subsequently, 706 g of the powder B, 14g of nitric acid-acidic alumina binder and 800 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on the catalyst Z1, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby to obtain a catalyst B provided with a coat formed on the catalyst Z1 and having a weight of 72 g per one liter of the monolithic substrate. The catalyst B carried 7.06 g of Pd per one liter of the monolithic substrate.



Additionally, 588 g of the powder G, 12g of nitric acid-acidic alumina binder and 600 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on the catalyst B, so that the walls of the cells were coated with the slurry.

- 5 The thus coated catalyst was dried and fired thereby to obtain a catalyst BG (shown in Table 2) at in an amount of 60 g per one liter of the monolithic substrate. The catalyst BG carried 3.53 g per one liter of the monolithic substrate. The catalyst BG took a three-layer structure as shown in Fig. 3.

- 10 In the column of "HC adsorbing layer" in Table 2, " $\beta(=25)$ " indicates the fact that the HC adsorbing layer contained  $\beta$ -zeolite (having a Si/2Al ratio of 25).

[Construction of Exhaust Gas Purifying System]

- An exhaust gas purifying system of Example 8 was  
15 constructed by disposing the catalyst BG in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the (NOx reducing) catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst BG and  
20 located at the position of the catalyst 2.

EXAMPLES 9 to 12

[Preparation of Catalyst]

- Catalysts CG, DG, EG and FG (shown in Table 2) corresponding respectively to Examples 9, 10, 11 and 12 were  
25 obtained repeating the above preparation operation for the catalyst BG with the exception that the powder B was replaced with other powders shown in Table 2, respectively.

[Construction of Exhaust Gas Purifying System]

- Each of exhaust gas purifying systems of Examples 9, 10,  
30 11 and 12 (shown in Table 2) was constructed by disposing the catalyst CG, DG, EG or FG in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the (NOx



reducing) catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst CG, DG, EG or FG and located at the position of the catalyst 2.

### EXAMPLE 13

#### 5 [Preparation of Catalyst]

$\beta$ -Zeolite ( $\text{Si}/2\text{Al} = 25$ ) in an amount of 900 g was mixed with 100 g of silica sol and 1000 g of pure water, followed by pulverizing, thereby forming a slurry. The slurry was coated on a cordierite ceramic honeycomb-type monolithic substrate having a  
10 volume of 1.3 liters and 900 cells per square inch and having a thickness of walls (defining each cell) of 4 mil, so that the walls of the cells were coated with the slurry. The thus coated substrate was dried and then fired thereby to obtain a catalyst Z1 having 100 g of a zeolite coat per one liter of the monolithic substrate.

15 Subsequently, 706 g of the powder B, 706 g of the powder A, 28 g of nitric acid-acidic alumina binder and 1500 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on the catalyst Z1, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby  
20 to obtain a catalyst BA provided with a coat formed on the catalyst Z1 and having a weight of 144 g per one liter of the monolithic substrate. The catalyst BA carried 14.12 g of Pd per one liter of the monolithic substrate.

25 Additionally, 588 g of the powder H, 12g of nitric acid-acidic alumina binder and 600 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on the catalyst BA, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby to obtain a catalyst BAH (shown in Table 2) provided with a coat formed on the  
30 catalyst BA and having a weight of 60 g per one liter of the monolithic substrate. The catalyst BAH carried 3.53 g per one liter of the monolithic substrate. The catalyst BAH took a three-layer structure as shown in Fig. 3.



In the column of "First layer" in Table 2, "B+A" indicates the fact that the First layer contained a mixture of the powders B and A.

[Construction of Exhaust Gas Purifying System]

- 5           An exhaust gas purifying systems of Example 13 was constructed by disposing the catalyst BAH in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the (NO<sub>x</sub> reducing) catalyst N1 was disposed in the  
10 exhaust gas passageway 10a downstream of the catalyst BAH and located at the position of the catalyst 2.

EXAMPLES 14 to 19

[Preparation of Catalyst]

- 15           Catalysts BAI, BAJ, BAK, BAL, BAM and BAN (shown in Table 2) corresponding respectively to Examples 14, 15, 16, 17, 18 and 19 were obtained repeating the above preparation operation for the catalyst BAH with the exception that  $\beta$ -zeolite ( $\text{Si}/2\text{Al} = 25$ ) and the powder H were replaced with other HC adsorbing materials and other powders shown in Table 2, respectively.

- 20           [Construction of Exhaust Gas Purifying System]

- Each of exhaust gas purifying systems of Examples 14, 15, 16, 17, 18 and 19 was constructed by disposing the catalyst BAI, BAJ, BAK, BAL, BAM or BAN in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the  
25 position of the catalyst 1, as shown in Fig. 6. Additionally, the (NO<sub>x</sub> reducing) catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst BAI, BAJ, BAK, BAL, BAM or BAN and located at the position of the catalyst 2.

EXAMPLE 20

- 30           [Preparation of Catalyst]

$\beta$ -Zeolite ( $\text{Si}/2\text{Al} = 25$ ) in an amount of 900 g was mixed with 100 g of silica sol and 1000 g of pure water, followed by pulverizing, thereby forming a slurry. The slurry was coated on a





cordierite ceramic honeycomb-type monolithic substrate having a volume of 1.3 liters and 900 cells per square inch and having a thickness of walls (defining each cell) of 4 mil, so that the walls of the cells were coated with the slurry. The thus coated substrate was  
5 dried and then fired thereby to obtain a catalyst Z2 having 50 g of a zeolite coat per one liter of the monolithic substrate.

Then, 471 g of the powder O, 9 g of nitric acid-acidic alumina binder and 500 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on an upstream  
10 section of the catalyst Z2, so that the walls of the cells were coated with the slurry to form an upstream layer. The upstream section was located upstream relative to flow direction of exhaust gas to be flown through the cells, and had a length of 1/4 of the total length of the monolithic substrate. The catalyst Z2 was dried and fired thereby to  
15 obtain a catalyst O1 provided with a coat formed on the catalyst Z2 and having a weight of 48 g per one liter of the monolithic substrate. The catalyst O1 carried 7.06 g of Pd per one liter of the monolithic substrate.

Subsequently, 706 g of the powder B, 706 g of the powder A,  
20 28 g of nitric acid-acidic alumina binder and 1000 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on a downstream section of the catalyst O1, so that the walls of the cells were coated with the slurry. The upstream section was located downstream of the upstream section relative to the flow  
25 direction of exhaust gas to be flown through the cells, and had a length of 3/4 of the total length of the monolithic substrate. The thus coated catalyst was dried and fired thereby to obtain a catalyst OBA provided with a coat formed on the downstream section of the catalyst O1 and having a weight of 144 g per one liter of the  
30 monolithic substrate. The catalyst OBA carried totally 21.18 g of Pd per one liter of the monolithic substrate.

Additionally, 588 g of the powder L, 12g of nitric acid-acidic alumina binder and 600 g of pure water were mixed and



pulverized thereby forming a slurry. The slurry was coated on the downstream side of the catalyst OBA, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby to obtain a catalyst OBAL (shown in Table 2) provided  
5 with a coat formed on the catalyst OBA and having a weight of 60 g per one liter of the monolithic substrate. The catalyst OBAL carried 3.53 g of Rh per one liter of the monolithic substrate. The catalyst OBAL took a structure as shown in Fig. 4.

In the column of "Second layer" in Table 2, "B+A" indicates  
10 the fact that the Second layer contained a mixture of the powder B and the powder A. In the column of "Third layer" in Table 2, "L" indicates the fact that the Third layer contained the powder L.

The HC adsorbing layer, the First layer, the Second layer and the Third layer shown in Table 2 are correspondingly illustrated  
15 in Fig. 4.

#### [Construction of Exhaust Gas Purifying System]

An exhaust gas purifying systems of Example 20 was constructed by disposing the catalyst OBAL in the exhaust gas passageway 10a extending from the internal combustion engine 10  
20 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the (NO<sub>x</sub> reducing) catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst OBAL and located at the position of the catalyst 2.

#### EXAMPLES 21 to 25

##### 25 [Preparation of Catalyst]

Catalysts PBBK, QBCJ, RBDI, SBEH and OBFG (shown in Table 2) corresponding respectively to Examples 21, 22, 23, 24 and 25 were obtained repeating the above preparation operation for the catalyst BAH with the exception that  $\beta$ -zeolite ( $\text{Si}/2\text{Al} = 25$ ), the  
30 powder O (in the first layer), the powders B and A (in the second layer) and/or the powder L (in the third layer) were replaced with other HC adsorbing materials and other powders shown in Table 2, respectively.



In the column of "Second layer" in Table 2, "2 x B" indicates the fact that the Second layer contained two the powder B of an amount of two times of that in the catalyst OBAL was contained in the Second layer.

5 [Construction of Exhaust Gas Purifying System]

Each of exhaust gas purifying systems of Examples 21 to 25 was constructed by disposing the catalyst PBBK to OBFG in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as  
10 shown in Fig. 6. Additionally, the (NOx reducing) catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst PBBK to OBFG and located at the position of the catalyst 2.

EXAMPLE 26

[Preparation of Catalyst]

15  $\beta$ -Zeolite (Si/2Al = 25) in an amount of 900 g was mixed with 100 g of silica sol and 1000 g of pure water, followed by pulverizing, thereby forming a slurry. The slurry was coated on a cordierite ceramic honeycomb-type monolithic substrate having a volume of 1.3 liters and 900 cells per square inch and having a  
20 thickness of walls (defining each cell) of 4 mil, so that the walls of the cells were coated with the slurry. The thus coated substrate was dried and then fired thereby to obtain a catalyst Z2 having 50 g of a zeolite coat per one liter of the monolithic substrate.

Then, 706 g of the powder B and 14g of nitric acid-acidic  
25 alumina binder and 1000 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on the catalyst Z2, so that the walls of the cells were coated with the slurry. The thus coated catalyst Z2 was dried and fired thereby to obtain a catalyst B2 provided with a coat formed on the catalyst Z2 and having a  
30 weight of 72 g per one liter of the monolithic substrate. The catalyst B2 carried 7.06 g of Pd per one liter of the monolithic substrate.

Subsequently, 588 g of the powder G, 12 g of nitric acid-acidic alumina binder and 600 g of pure water were mixed and



pulverized thereby forming a slurry. The slurry was coated on the catalyst B2, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby to obtain a catalyst BG provided with a coat formed on the catalyst B2 and  
5 having a weight of 60 g per one liter of the monolithic substrate. The catalyst BG carried 3.53 g of Rh per one liter of the monolithic substrate.

Additionally, 618 g of the powder T, 530 g of the powder U, 88 g of the powder V, 20 g of sodium hydroxide (calculated as  $\text{Na}_2\text{O}$ ),  
10 20 g of barium acetate (calculated as  $\text{BaO}$ ), 14 g of nitric acid-acidic alumina binder and 1500 g of pure water were mixed, followed by pulverizing, thereby forming a slurry. This slurry was coated on the catalyst BG, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby to obtain a  
15 catalyst BGN1 provided with a coat formed on the catalyst BG and having a weight of 147 g per one liter of the monolithic substrate. The catalyst BGN1 carried 12.0 g of Pd, 3.18 g of Pt and 3.88 g of Rh per one liter of the monolithic substrate. The catalyst BGN1 took a structure shown in Fig. 5.

20 The HC adsorbing layer, the First layer, the Second layer and the Third layer shown in Table 2 are correspondingly illustrated in Fig. 5.

#### [Construction of Exhaust Gas Purifying System]

An exhaust gas purifying systems of Example 26 was  
25 constructed by disposing the catalyst BGN1 in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the ( $\text{NO}_x$  reducing) catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst BGN1 and  
30 located at the position of the catalyst 2.

#### EXAMPLE 27

##### [Preparation of $\text{NO}_x$ reducing Catalyst]

11



A (NOx reducing) catalyst N2 was obtained by repeating the above preparation operation for the catalyst N1 in Example 1 with the exception that sodium hydroxide was replaced with magnesium acetate, in which 10g of MgO and 10 g of BaO were carried per one liter of the monolithic substrate.

[Construction of Exhaust Gas Purifying System]

An exhaust gas purifying systems of Example 27 was constructed by disposing the catalyst AG1 in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the NOx reducing catalyst N2 was disposed in the exhaust gas passageway 10a downstream of the catalyst AG1 and located at the position of the catalyst 2.

EXAMPLE 28

[Construction of Exhaust Gas Purifying System]

An exhaust gas purifying systems of Example 28 was constructed by disposing the catalyst BGN1 in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the NOx reducing catalyst N2 was disposed in the exhaust gas passageway 10a downstream of the catalyst BA1 and located at the position of the catalyst 2.

EXAMPLE 29

[Construction of Exhaust Gas Purifying System]

An exhaust gas purifying systems of Example 29 was constructed by disposing the catalyst BAH in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the NOx reducing catalyst N2 was disposed in the exhaust gas passageway 10a downstream of the catalyst BAH and located at the position of the catalyst 2.

EXAMPLE 30

[Construction of Exhaust Gas Purifying System]



An exhaust gas purifying systems of Example 30 was constructed by disposing the catalyst OBFG in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6.

5 Additionally, the NOx reducing catalyst N2 was disposed in the exhaust gas passageway 10a downstream of the catalyst OBFG and located at the position of the catalyst 2.

#### COMPARATIVE EXAMPLE 1

[Preparation of Three-way catalyst]

10 The powder T in an amount of 565 g, 226 g of the powder F, 10 g of barium acetate (calculated as BaO), 9 g of nitric acid-acidic alumina binder and 1000 g of pure water were mixed, followed by pulverizing, thereby forming a slurry. This slurry was coated on a cordierite ceramic honeycomb-type monolithic substrate having a

15 volume of 1.3 liters and 900 cells per square inch and having a thickness of walls (defining each cell) of 2 mil, so that the walls of the cells were coated with the slurry. The thus coated monolithic substrate was dried and fired thereby to obtain a catalyst T0 provided with a coat formed on the monolithic substrate and having

20 a weight of 90 g per one liter of the monolithic substrate.

Subsequently, 128 g of the powder V, 200 g of  $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$  powder, 12 g of nitric acid-acidic alumina binder and 500 g of pure water were mixed, followed by pulverizing, thereby forming a slurry. This slurry was coated on the catalyst T0 so that the walls of the

25 cells were coated with the slurry, followed by drying and firing, thereby to obtain a catalyst T1 provided with a coat formed on the catalyst T0 and having a weight of 34 g per one liter of the monolithic substrate. The catalyst T1 carried 5.65 g of Pd and 0.51 g of Rh per one liter of the monolithic substrate. The catalyst T1 took

30 such a structure in which two layers of coat were formed on the monolithic substrate.

[Construction of Exhaust Gas Purifying System]



An exhaust gas purifying systems of Comparative Example 1 was constructed by disposing the catalyst T1 in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the NOx reducing catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst T1 and located at the position of the catalyst 2.

#### EVALUATION OF PERFORMANCE OF EXHAUST GAS PURIFYING CATALYST

10 Evaluation test (for emission performance) was conducted on the exhaust gas purifying systems of Examples and Comparative Examples, using an evaluation engine system as shown in Fig. 6. For the evaluation test, each exhaust gas purifying system was incorporated in the evaluation engine system including the engine 15 10 which was a cylinder direct injection internal combustion engine having a displacement of 1.8 liters and produced by Nissan Motor Co., Ltd.

Prior to the evaluation test, the catalysts (corresponding to the catalyst 1 in Fig. 6) of Examples and Comparative Example 20 underwent a durability test in which each catalyst was connected to an internal combustion engine produced by Nissan Motor Co., Ltd. In the durability test, the engine was operated under the following test conditions:

Displacement of the engine: 3,000 cc;  
25 Fuel: "Nisseki Dasshu Gasoline" produced by Nippon Oil Co., Ltd. and having a Pb content of 0 mg/usg (US gallon) and a S content of not more than 30 ppm;

Temperature of gas to be supplied to the catalyst: 650 °C;  
and

30 Time of operation of the engine: 50 hours.

Then, the catalyst 1 undergone the durability test was subjected to the emission performance evaluation test conducted under a test mode "FTP-75 (LA-4) mode" employed in the Unites



States of America. In this test, the exhaust gas purifying system was incorporated in the evaluation engine system of Fig. 6, in the catalyst 1 was installed at its predetermined position shown in Fig. 6. The engine was arranged such that fuel was directly injected into each cylinder. In the emission performance evaluation test, the catalyst 1 and the catalyst 2 had the following volumes:

Catalyst 1: 1.3 liters

Catalyst 2: 1.3 liters

In the emission performance evaluation test, a concentration A of gas components (HC, CO and NOx) in exhaust gas from the engine in a state where no exhaust gas purifying system was provided was measured, and a concentration B in exhaust gas emitted from the catalyst 2 (NOx reducing catalyst) in Fig. 6 was measured, thereby obtaining a "remaining rate (%)" of the gas components, shown in Table 3. The remaining rate (%) was calculated by [(the concentration B of the gas component / the concentration A of the gas component) x 100], in which the concentrations were measured as "ppm"

As apparent from the above, according to the present invention, by virtue of the catalytic layer for functioning to produce hydrogen (H<sub>2</sub>), the produced hydrogen is used as reducing agent. As a result, the catalyst of the present invention can reduce and remove NOx in exhaust gas at a high efficiency under the oxygen-excessive atmosphere of exhaust gas and effectively removing HC and CO particularly during a low temperature engine operation immediately after engine starting, while obtaining a high fuel economy improvement effect upon making lean-burn operation of the engine.

The entire contents of Japanese Patent Applications P11-336839 (filed November 26, 1999) and P2000-342550 (filed November 9, 2000) are incorporated herein by reference.

Although the invention has been described above by reference to certain embodiments of the invention, the invention is not limited to the embodiments and examples described above.





Modifications and variations of the embodiments and examples described above will occur to those skilled in the art, in light of the above teachings. The scope of the invention is defined with reference to the following claims.

5 INDUSTRIAL APPLICABILITY

As discussed above, the exhaust gas purifying catalyst according to the present invention can be applied to reduce and remove NO<sub>x</sub> in exhaust gas at a high efficiency under the oxygen-excessive atmosphere of exhaust gas and effectively  
10 removing HC and CO, maintaining a high fuel economy improvement effect under lean-burn operation.



TABLE 1

Powder (catalyst component)	Metal carried		Carrier
	Kind	Concentration (%)	
A	Pd	10.0	CeO <sub>2</sub>
B	Pd	10.0	Zr <sub>0.1</sub> Ce <sub>0.9</sub> O <sub>2</sub>
C	Pd	10.0	Zr <sub>0.2</sub> Ce <sub>0.8</sub> O <sub>2</sub>
D	Pd	10.0	Zr <sub>0.5</sub> Ce <sub>0.5</sub> O <sub>2</sub>
E	Pd	10.0	Zr <sub>0.9</sub> Ce <sub>0.1</sub> O <sub>2</sub>
F	Pd	5.0	CeO <sub>2</sub>
G	Rh	6.0	Ca <sub>0.2</sub> Zr <sub>0.8</sub> O <sub>2</sub>
H	Rh	6.0	Mg <sub>0.1</sub> Zr <sub>0.9</sub> O <sub>2</sub>
I	Rh	6.0	Ba <sub>0.1</sub> Zr <sub>0.9</sub> O <sub>2</sub>
J	Rh	6.0	Sr <sub>0.2</sub> Zr <sub>0.8</sub> O <sub>2</sub>
K	Rh	6.0	Ca <sub>0.1</sub> Mg <sub>0.1</sub> Zr <sub>0.8</sub> O <sub>2</sub>
L	Rh	6.0	Ca <sub>0.1</sub> Ba <sub>0.05</sub> Mg <sub>0.05</sub> Zr <sub>0.8</sub> O <sub>2</sub>
M	Rh	6.0	Ca <sub>0.01</sub> Zr <sub>0.99</sub> O <sub>2</sub>
N	Rh	6.0	Ca <sub>0.5</sub> Zr <sub>0.5</sub> O <sub>2</sub>
O	Pd	15.0	Al <sub>2</sub> O <sub>3</sub>
P	Pd	15.0	Ce(3wt.%) - Al <sub>2</sub> O <sub>3</sub>
Q	Pd	15.0	Zr(3wt.%) - Al <sub>2</sub> O <sub>3</sub>
R	Pd	15.0	La(3wt.%) - Al <sub>2</sub> O <sub>3</sub>
S	Pd	15.0	Zr(10wt.%) - Al <sub>2</sub> O <sub>3</sub>
T	Pd	8.0	Al <sub>2</sub> O <sub>3</sub>
U	Pt	6.0	Al <sub>2</sub> O <sub>3</sub>
V	Rh	4.0	Al <sub>2</sub> O <sub>3</sub>



TABLE 2

Catalyst	Structure of catalyst	Substance carried				HC adsorbing layer	First layer	Second layer	Third layer
		Pd	Pt	Rh	Alkali metal oxide	Alkaline earth metal oxide			
AG1	Fig.3	7.06	-	3.53	-	-	A	G	-
AG2	Fig.3	7.06	-	3.53	-	-	A	G	-
AG3	Fig.3	7.06	-	3.53	-	-	A	G	-
AG4	Fig.3	7.06	-	3.53	-	-	A	G	-
AG5	Fig.3	7.06	-	3.53	-	-	A	G	-
AG6	Fig.3	7.06	-	3.53	-	-	A	G	-
AG7	Fig.3	7.06	-	3.53	-	-	A	G	-
BG	Fig.3	7.06	-	3.53	-	-	A	G	-
CG	Fig.3	7.06	-	3.53	-	-	B	G	-
DG	Fig.3	7.06	-	3.53	-	-	C	G	-
EG	Fig.3	7.06	-	3.53	-	-	D	G	-
FG	Fig.3	7.06	-	3.53	-	-	E	G	-
BAH	Fig.3	14.12	-	3.53	-	-	F	G	-
BAI	Fig.3	14.12	-	3.53	-	-	B+A	H	-
BAJ	Fig.3	14.12	-	3.53	-	-	B+A	I	-
BAK	Fig.3	14.12	-	3.53	-	-	B+A	J	-
BAL	Fig.3	14.12	-	3.53	-	-	B+A	K	-
BAM	Fig.3	14.12	-	3.53	-	-	B+A	L	-
BAN	Fig.3	14.12	-	3.53	-	-	B+A	M	-
OBAL	Fig.4	21.18	-	3.53	-	-	B+A	N	-
PBBK	Fig.4	21.18	-	3.53	-	-	O	B+A	L
QBCJ	Fig.4	21.18	-	3.53	-	-	P	2×B	K
RBDI	Fig.4	21.18	-	3.53	-	-	O	B+C	J
SBEH	Fig.4	21.18	-	3.53	-	-	R	B+D	I
OBFG	Fig.4	21.18	-	3.53	-	-	S	B+E	H
BGNI	Fig.5	12.0	3.18	3.88	(Na <sub>2</sub> O) <sub>2</sub>	(BaO) <sub>20</sub>	O	B+F	G
N1	Single layer	4.94	3.18	0.35	(Na <sub>2</sub> O) <sub>2</sub>	(BaO) <sub>20</sub>	B	G	T+U+V
N2	Single layer	4.94	3.18	0.35	(MgO) <sub>10</sub>	(BaO) <sub>10</sub>			
T1	Two layers	5.65	-	0.51	-	(BaO) <sub>10</sub>			



TABLE 3

	Installation position		Remaining rate (%)		
	Catalyst 1	Catalyst 2	HC	CO	NOx
Example 1	AG1	N1	1.3	1.9	2.4
Example 2	AG2	N1	1.2	1.8	2.2
Example 3	AG3	N1	1.1	1.7	2.1
Example 4	AG4	N1	1.1	1.8	1.9
Example 5	AG5	N1	1.2	1.8	2.0
Example 6	AG6	N1	1.2	1.7	2.0
Example 7	AG7	N1	1.2	1.8	2.1
Example 8	BG	N1	1.2	1.7	1.9
Example 9	CG	N1	1.3	1.6	2.1
Example 10	DG	N1	1.3	1.6	2.2
Example 11	EG	N1	1.2	1.7	2.0
Example 12	FG	N1	1.2	1.8	2.1
Example 13	BAH	N1	1.1	1.9	1.9
Example 14	BAI	N1	1.1	1.8	1.9
Example 15	BAJ	N1	1.1	1.8	2.0
Example 16	BAK	N1	1.2	1.8	2.0
Example 17	BAL	N1	1.1	1.9	2.1
Example 18	BAM	N1	1.2	1.8	2.1
Example 19	BAN	N1	1.3	1.8	2.2
Example 20	OBAL	N1	1.4	2.0	2.2
Example 21	PBBK	N1	1.2	1.8	2.1
Example 22	QBCJ	N1	1.1	1.9	1.9
Example 23	RBDI	N1	1.1	1.8	1.9
Example 24	SBEH	N1	1.1	1.8	2.0
Example 25	OBFG	N1	1.2	1.8	2.0
Example 26	BGN1	N1	1.3	2.4	2.2
Example 27	AG1	N2	1.2	1.7	2.0
Example 28	BG1	N2	1.3	1.6	2.1
Example 29	BAH	N2	1.2	1.7	2.1
Example 30	OBFG	N2	1.1	1.8	2.0
Comp. example 1	TI	N1	4.2	7.1	7.3





CLAIMS

1. An exhaust gas purifying catalyst comprising:  
a monolithic substrate;  
a HC adsorbing layer for adsorbing hydrocarbons (HC),  
5 said HC adsorbing layer containing zeolite and being formed on said monolithic substrate;  
a catalytic layer for producing hydrogen (H<sub>2</sub>) and reducing NO<sub>x</sub>, said catalytic layer functioning to produce hydrogen (H<sub>2</sub>) from at least one of hydrocarbons and carbon monoxide (CO) and to  
10 reduce nitrogen oxides (NO<sub>x</sub>) with the produced hydrogen and at least one of hydrocarbons and carbon monoxide in exhaust gas, said catalytic layer being formed on said HC adsorbing layer.
2. An exhaust gas purifying catalyst as claimed in Claim 1,  
15 wherein said exhaust gas purifying catalyst is for purifying exhaust gas discharged from an internal combustion engine, wherein said HC adsorbing layer contains zeolite and functions to adsorb hydrocarbons during a cold operation of the engine and to release adsorbed hydrocarbons during a warm-up operation of the engine,  
20 wherein said catalytic layer functions to produce hydrogen from hydrocarbons released from said HC adsorbing layer and from at least one of hydrocarbons and carbon monoxide discharged from the engine after the warm-up operation and to reduce NO<sub>x</sub> with produced hydrogen and at least hydrocarbons and carbon monoxide  
25 in exhaust gas.
3. An exhaust gas purifying catalyst as claimed in Claim 1 or 2, wherein said catalytic layer contains a H<sub>2</sub> producing catalyst component for functioning to produce hydrocarbons, and a NO<sub>x</sub>  
30 reducing catalyst component for functioning to reduce nitrogen oxides, said H<sub>2</sub> producing catalyst component being disposed on said HC adsorbing layer and including a HC reforming catalyst component functioning to reform hydrocarbons so as to produce



hydrogen and a CO reforming catalyst component functioning to make steam reforming of carbon monoxide, said HC reforming catalyst component containing cerium oxide carrying palladium, said CO reforming catalyst component containing zirconium oxide carrying rhodium.

4. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 3, wherein said catalytic layer further includes an upstream layer formed at an upstream section of said exhaust gas purifying catalyst, said upstream section being located upstream of said HC reforming catalyst component layer and said CO reforming catalyst component layer relative to flow direction of exhaust gas, said upstream layer containing alumina carrying palladium.

5. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 4, wherein said zirconium oxide carrying rhodium contains alkaline earth and has a composition represented by the following formula (A):



where X is an alkaline earth metal selected from the group consisting of magnesium, calcium, strontium and barium; a and b are ratios of atoms of elements; and c is a number of oxygen atoms required for satisfying valences of X and Zr, in which a is within a range of from 0.01 to 0.5, b is within a range of from 0.5 to 0.99, and  $a+b = 1.0$ .

6. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 5, wherein a NOx reducing catalyst component functioning to reduce nitrogen oxides is contained in at least one of said HC adsorbing layer, said HC reforming layer, said CO reforming layer and said upstream layer containing alumina carrying palladium.



7. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 6, wherein a NO<sub>x</sub> reducing catalyst component functioning to reduce nitrogen oxides is contained in at least one of said HC adsorbing layer, said HC reforming layer, said CO reforming layer and said upstream layer containing alumina carrying palladium, said NO<sub>x</sub> reducing catalyst component containing at least one selected from the group consisting of palladium, platinum, rhodium, alumina, alkali metal and alkaline earth metal.
8. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 7, wherein said zeolite contains H-type  $\beta$ -zeolite having a Si/2Al ratio ranging from 10 to 500.
9. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 8, wherein said zeolite contains H-type  $\beta$ -zeolite and at least one of MFI, Y-type zeolite, USY-type zeolite and mordenite.
10. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 9, wherein said zeolite contains at least one selected from the group consisting of palladium, magnesium, calcium, strontium, barium, silver, yttrium, lanthanum, cerium, neodymium, phosphorus, boron and zirconium.
11. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 10, wherein a NO<sub>x</sub> reducing catalyst component functioning to reduce nitrogen oxides is contained in at least one of said HC adsorbing layer, said HC reforming layer, said CO reforming layer and said upstream layer containing alumina carrying palladium, said NO<sub>x</sub> reducing catalyst component containing at least one selected from the group consisting of alkali metal and alkaline earth metal, said NO<sub>x</sub> reducing catalyst



component containing at least one selected from the group consisting of potassium, cesium, magnesium, calcium and barium.

12. An exhaust gas purifying catalyst as claimed in Claim 3,  
5 wherein said HC reforming catalyst component and said CO reforming catalyst are mixed to form a single layer disposed on said monolithic substrate on said HC adsorbing layer.

13. An exhaust gas purifying catalyst as claimed in Claim 3,  
10 wherein said HC reforming catalyst component forms a first layer disposed on said monolithic substrate, and said CO reforming catalyst forms a second layer, said second layer being formed on said first layer.

14. An exhaust gas purifying catalyst as claimed in Claim 3,  
15 wherein said HC reforming catalyst component forms a first layer disposed on said monolithic substrate, and said CO reforming catalyst component forms a second layer, said second layer being formed downstream of said first layer relative to flow direction of  
20 exhaust gas.

15. An exhaust gas purifying system for an internal combustion engine, comprising:  
an exhaust gas purifying catalyst including  
25 a monolithic substrate,  
a HC adsorbing layer for adsorbing hydrocarbons (HC), said HC absorbing layer being formed on said monolithic substrate, and  
a catalytic layer for producing hydrogen (H<sub>2</sub>) and  
30 reducing NO<sub>x</sub>, said catalytic layer functioning to produce hydrogen (H<sub>2</sub>) from at least one of hydrocarbons and carbon monoxide (CO) and to reduce nitrogen oxides (NO<sub>x</sub>) with the produced hydrogen and





at least one of hydrocarbons and carbon monoxide in exhaust gas, said catalytic layer being formed on said HC adsorbing layer; and

- 5 a device for controlling combustion in the engine to produce exhaust gas, to be brought into contact with said catalytic layer, having a composition meeting a relation [(a concentration of hydrogen / a concentration of total reducing components)  $\geq$  0.3].

16. A method of producing an exhaust gas purifying catalyst, comprising:

- 10 preparing a monolithic substrate;  
forming a HC adsorbing layer on said monolithic layer, to adsorb hydrocarbons (HC); and  
forming a catalytic layer on said HC adsorbing layer, to produce hydrogen (H<sub>2</sub>) and reduce NO<sub>x</sub>, said catalytic layer  
15 functioning to produce hydrogen (H<sub>2</sub>) from at least one of hydrocarbons and carbon monoxide (CO) and to reduce nitrogen oxides (NO<sub>x</sub>) with the produced hydrogen and at least one of hydrocarbons and carbon monoxide in exhaust gas.



FIG.1

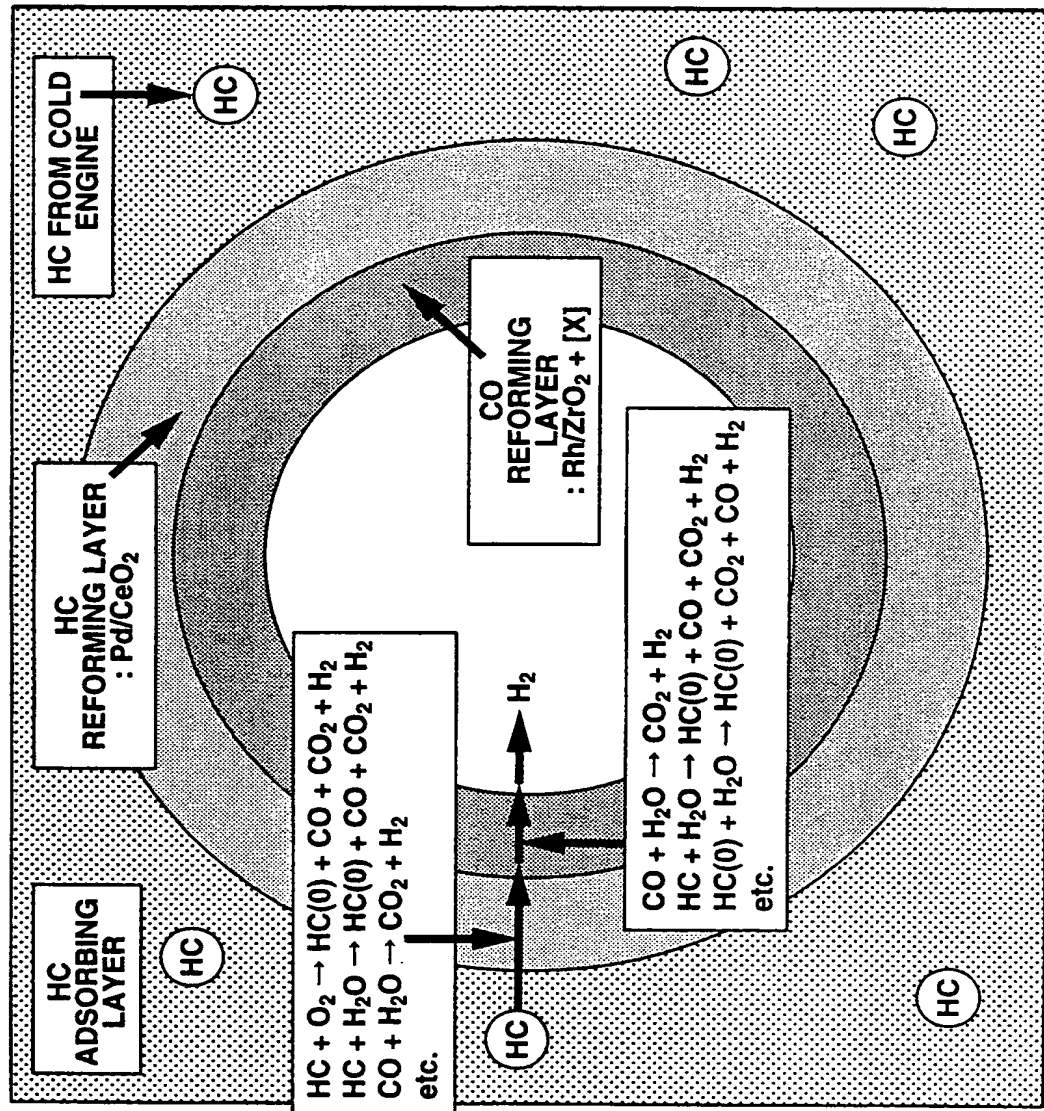




FIG.2

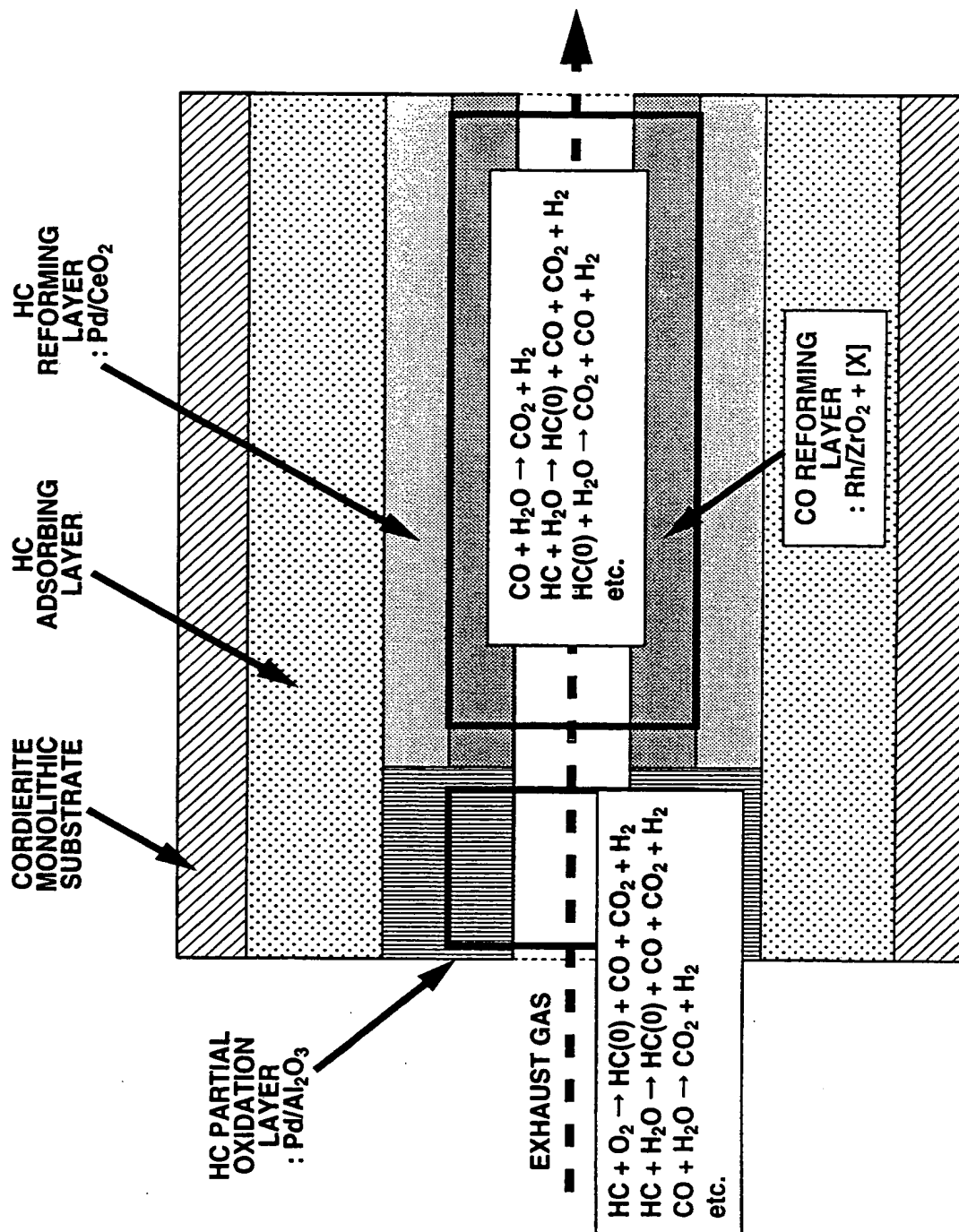




FIG.3

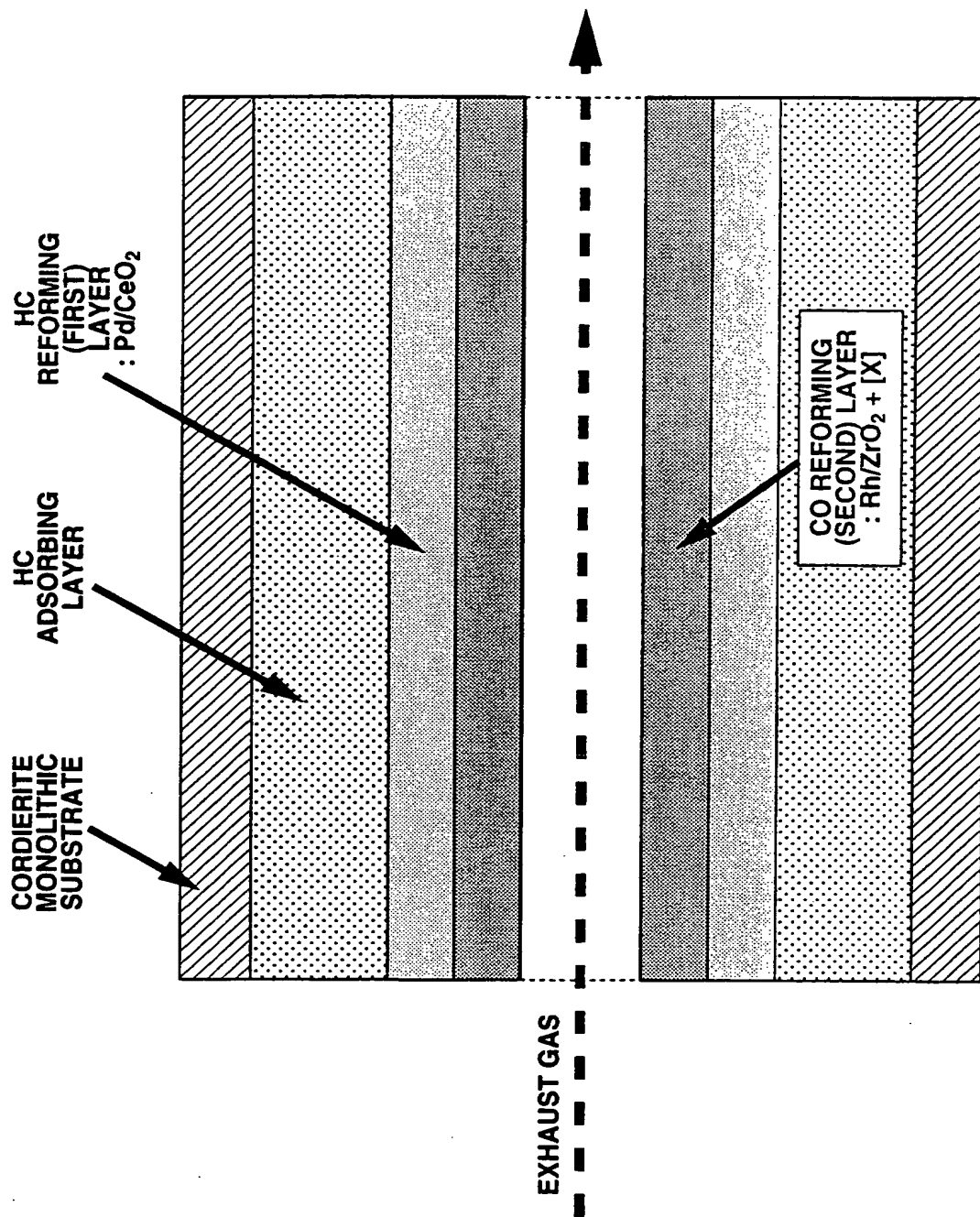






FIG.4

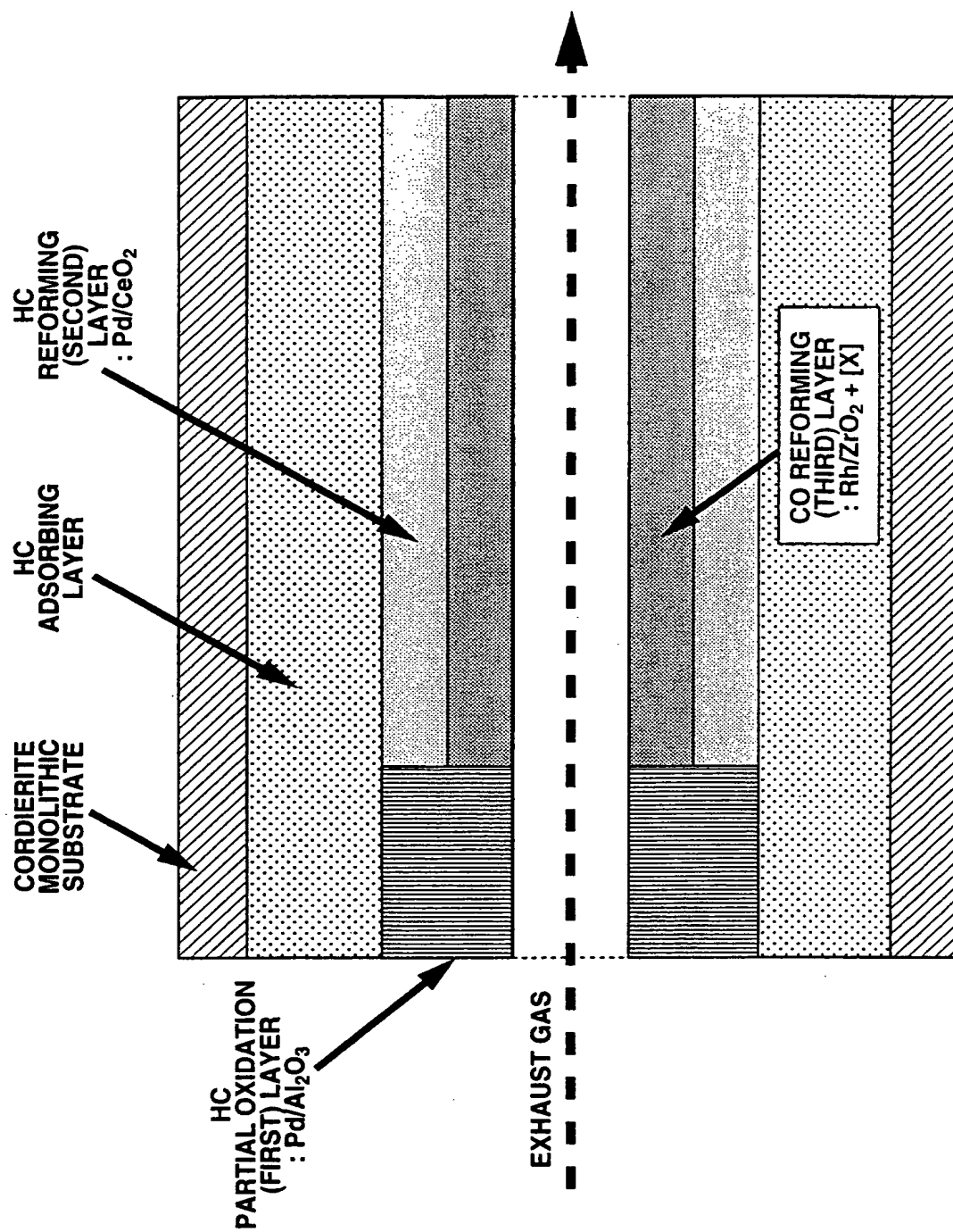




FIG.5

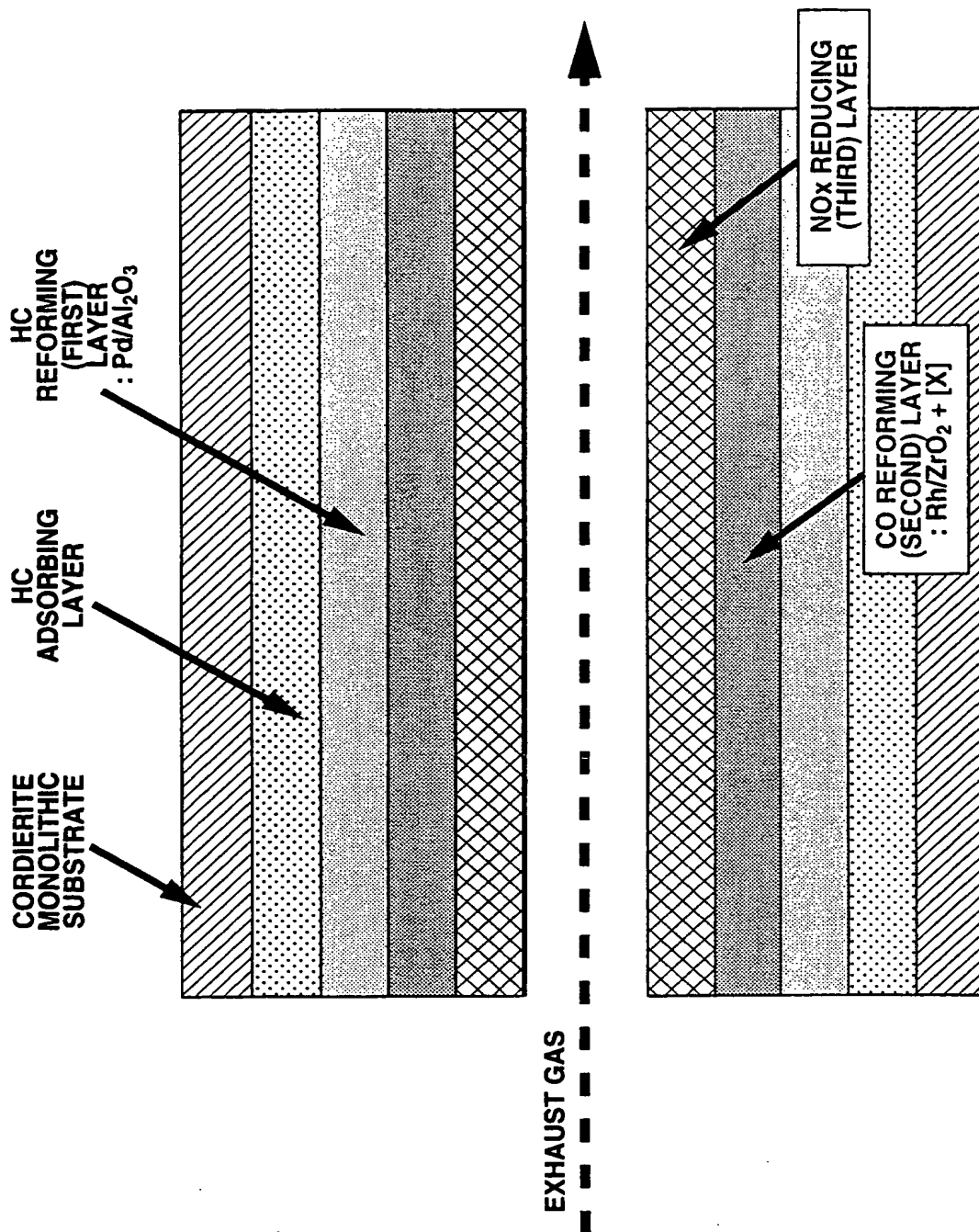
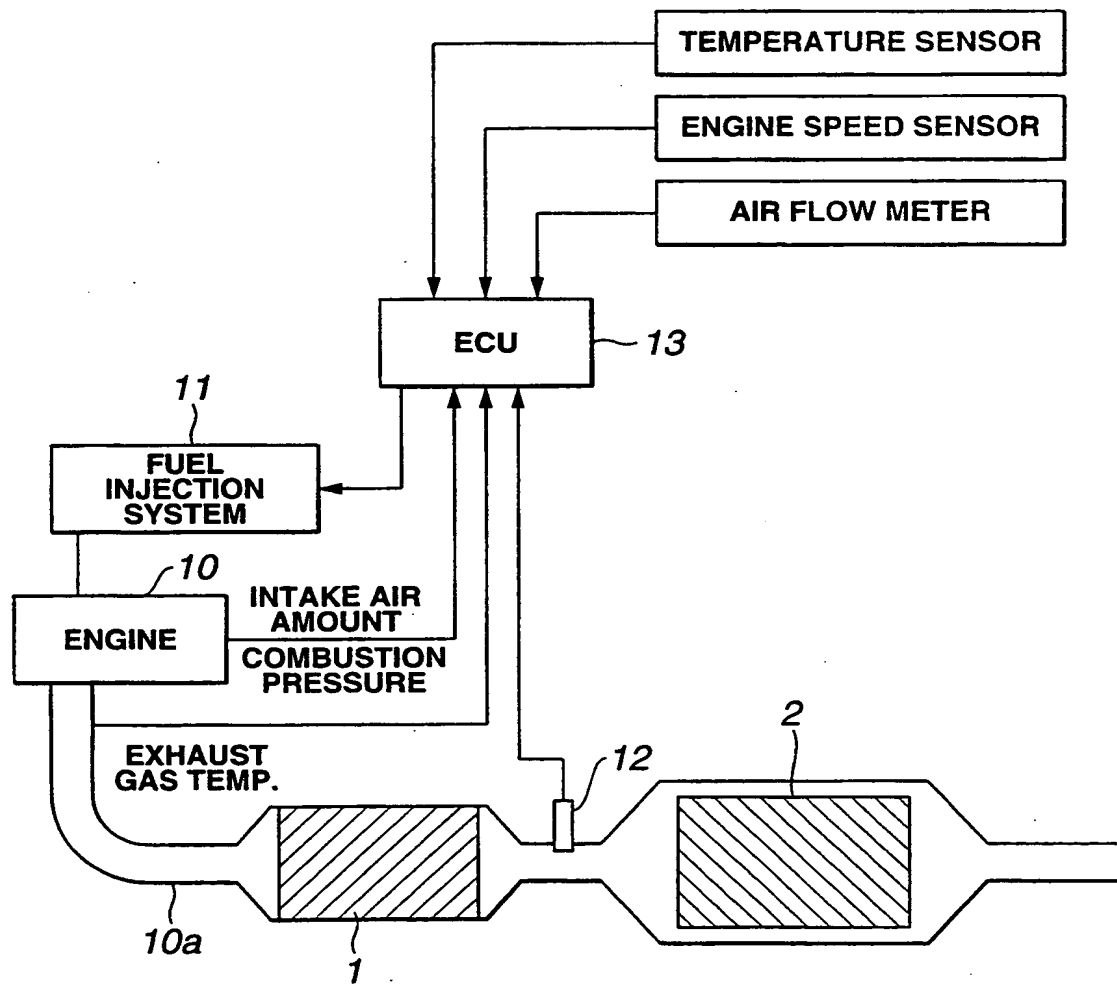




FIG.6





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# INTERNATIONAL SEARCH REPORT

International Application No.  
JP 00/08180

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 B01D53/94 B01J29/04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 852 966 A (TOYOTA MOTOR CO LTD) 15 July 1998 (1998-07-15)  page 4, line 29 -page 8, column 29 page 17, line 18 -page 18, line 36; figures 12-16; examples 12-15,22	1,2,5-7, 11,12, 15,16
X	EP 0 782 880 A (NGK INSULATORS LTD) 9 July 1997 (1997-07-09)  page 3, line 32 -page 6, line 43; example 16; tables 1,2,4 page 14, line 17 - line 20; figure 1E  -/--	1-4, 6-10,12, 13,15,16

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

12 March 2001

Date of mailing of the international search report

16/03/2001

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# INTERNATIONAL SEARCH REPORT

International Application No.

JP 00/08180

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 676 912 A (SHARMA SANJAY B ET AL) 14 October 1997 (1997-10-14) column 2, line 56 - line 60 column 4, line 8 - line 52 column 8, line 52 -column 10, line 42 column 13, line 18 - line 6 -----	1-10,12, 16
X	EP 0 002 791 A (UNION CARBIDE CORP) 11 July 1979 (1979-07-11) page 3, paragraph 1 -page 6, paragraph 1 page 8, paragraph 3 page 11, paragraph 2 -----	1,2,6-8, 10,12



# INTERNATIONAL SEARCH REPORT

International Application No

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